

SPECIALIA

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Isolation of alkaloids from *Athrotaxis selaginoides*

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Summary. A novel series of alkaloids has been obtained from the Tasmanian plant *Athrotaxis selaginoides*, the first to be isolated from the plant family Taxodiaceae.

Athrotaxis selaginoides D. Don is a large tree, well-known in Tasmania under the local name of King Billy Pine for its valuable soft-wood timber¹. It belongs to the Taxodiaceae, a small family distinguished by the fact that the world's tallest and largest trees belong to it (*Sequoia sempervirens* and *Sequoiadendron giganteum* respectively), as well as the *Metasequoia*, known only from extensive fossil deposits until recently, when *M. glyptostrobis* was found growing in a very restricted area of China. No alkaloids have previously been isolated from the family, and specimens of the above-mentioned Californian and Chinese plants growing in the Hobart Botanic Gardens gave negative alkaloid tests. However, positive reactions have been recorded for the root-wood and root-bark of the American species *Taxodium distichum*² and for seeds of the Chinese species *Cunninghamia lanceolata*³.

The 3 *Athrotaxis* species are the only representatives of the family in the southern hemisphere, and are all endemic in Tasmania. *A. selaginoides*¹ is confined to the mountainous regions of western Tasmania, where some specimens grow up to 40 m high and are over 1000 years old. In the field, foliage and bark samples gave moderately strong alkaloid tests, but after collection, the test rapidly became weaker and disappeared completely after a few days: it appeared that the alkaloids present were being destroyed by enzyme action. This effect could be minimized by roughly comminuting the freshly collected material as rapidly as possible, then soaking it in methanol for some days before extraction. The methanol extracts were worked up by standard means, and yielded 2 crystalline bases, alkaloid A, C₁₈H₂₃NO₄, m.p. 62–63 °C, [α]_D^{21.5} + 166.7° (c=0.25 in CHCl₃), and alkaloid B, C₂₁H₂₇NO₅, m.p. 197–205 °C (decomp.), [α]_D²² – 24.7° (c=0.47 in CHCl₃). At least 6 other alkaloids are present in the same plant, some of which also occur in a 2nd species, *A. cupressoides*¹, a rather smaller tree growing at higher altitudes in central and western Tasmania. The 3rd species, *A. laxifolia*¹, is rare and may represent a hybrid of the other two. Several other alkaloids from *A. selaginoides* have been obtained pure, but have not yet been crystallized.

The PMR-spectrum of alkaloid A shows the presence of 2 methoxyl groups, and other data, including the IR and CMR spectra, indicate that the remaining 2 oxygens are in a lactone ring. The nitrogen is present in a tertiary amino group, since there are no exchangeable protons in the PMR spectrum and all 23 protons are accounted for as being attached to carbon in the CMR spectrum. The latter also gives evidence of 6 aromatic or olefinic carbons, 2 of which are quaternary; there is, however, only a 1-proton signal, a singlet, in the aromatic region of the PMR spectrum, and a 1-proton multiplet in the olefinic region.

Alkaloid B also gives spectroscopic evidence of the presence of 2 methoxyl groups, and the remaining oxygens are accounted for in an acetoxyl and hydroxyl group; the presence of the latter is confirmed by acetylation.

Alkaline hydrolysis of alkaloid B affords a dihydroxy compound which can be reacylated to a diacetoxyl derivative isomeric but not identical with the above-mentioned O-acetyl alkaloid B.

Structural studies on the *Athrotaxis* alkaloids are still in progress, but the spectroscopic and other evidence so far available suggest that they constitute a novel series of bases with no obvious structural relationship with those from other coniferous plants, such as cephalotaxine⁴, pinidine⁵ and taxine⁶.

- 1 W.M. Curtis, The Student's Flora of Tasmania, part 1, p.6. Tasmanian Government Printer, Hobart, Tas., 1956.
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- 3 J.J. Willaman and H.-L. Li, *Lloydia* 33, 15 (1970).
- 4 J.S. Glasby, in: *Encyclopedia of the Alkaloids*, vol.1, p.273. Plenum Press, London 1975.
- 5 J.S. Glasby, in: *Encyclopedia of the Alkaloids*, vol.2, p.1108. Plenum Press, London 1975.
- 6 J.S. Glasby, in: *Encyclopedia of the Alkaloids*, vol.2, p.1287. Plenum Press, London 1975.